

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-140279

(43)Date of publication of application : 25.05.1999

(51)Int.Cl.

C08L 63/00
C08G 59/68
C08K 5/15

(21)Application number : 09-316401

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(22)Date of filing : 31.10.1997

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JITSUMATSU TETSUJI

(54) ACTIVE ENERGY RAY-CURING TYPE COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain the subject composition having a low viscosity, providing a cured material more flexible than ever by including a specific oxetane compound, a specific epoxy group-containing compound and a cationic polymerization photoinitiator.

SOLUTION: The objective compound includes (A) an oxetane compound of the formula (R1 is methyl or ethyl),
(B) a compound having two or more epoxy groups in a

molecule and selected from an aromatic epoxide, an alicyclic epoxy compound or an aliphatic epoxy compound, (C) a cationic polymerization photoinitiator, preferably a diaryliodonium salt, a triarylsulfonium salt or the like and (D) optionally a monofunctional epoxy compound, an oxetane compound other than the

component A, a cation-reactive compound, an inorganic filler, a dyestuff, a pigment, a viscosity modifier, a photosensitizer or the like. As the containing proportion, the content of the component A is 5-99 pts.wt. based on 100 pts.wt. total amount of components A and B and the content of the component C is preferably 0.1-20 wt.% based on the total amount of the components A and B.



AN 1999:331466 CAPLUS
 DN 131:6072
 ED Entered STN: 28 May 1999
 TI Oxetane-containing active energy beam-curable compositions with low viscosity
 IN Igarashi, Ichiro; Sasaki, Hiroshi; Sanematsu, Tetsuji
 PA Toa Gosei Chemical Industry Co., Ltd., Japan
 SO Jpn. Kokai Tokkyo Koho, 6 pp.
 CODEN: JKXXAF
 DT Patent
 LA Japanese
 IC ICM C08L063-00
 ICS C08G059-68; C08K005-15
 CC 37-6 (Plastics Manufacture and Processing)
 Section cross-reference(s): 38

FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI JP 11140279	A	19990525	JP 1997-316401	19971031 <--
PRAI JP 1997-316401		19971031		

CLASS

PATENT NO.	CLASS	PATENT FAMILY CLASSIFICATION CODES
JP 11140279	ICM	C08L063-00
	ICS	C08G059-68; C08K005-15
	IPCI	C08L0063-00 [ICM,6]; C08G0059-68 [ICS,6]; C08K0005-15 [ICS,6]
	IPCR	C08G0059-00 [I,C*]; C08G0059-68 [I,A]; C08K0005-00 [I,C*]; C08K0005-15 [I,A]; C08L0063-00 [I,A]; C08L0063-00 [I,C*]

AB Title compns., giving cured products with good flexibility, contain 3-methyl-3-phenoxy-methyloxetane or 3-ethyl-3-phenoxy-methyloxetane (I), compds. containing ≥ 2 epoxy groups, and photo-cationic polymerization initiators. (Thus,) I, YD 128 (bisphenol A-type epoxy resin), and Cyacure UVI 6990 were mixed to give a composition with viscosity 23 mPa-s at 25°, which was irradiated with UV light to give a test piece showing tensile strength 95 kg/cm² and elongation 210%.

ST epoxy oxetane active energy beam curable; UV curable epoxy oxetane low viscosity; flexibility epoxy resin oxetane photocured

IT Polymerization catalysts
 (cationic; epoxy compound-oxetane active energy beam-curable compns. with low viscosity)

IT Polyethers, preparation
 Polyethers, preparation
 RL: IMF (Industrial manufacture); PRP (Properties); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)
 (epoxy, aromatic; epoxy compound-oxetane active energy beam-curable compns. with low viscosity)

IT Polymerization catalysts
 (photopolymn.; epoxy compound-oxetane active energy beam-curable compns. with low viscosity)

IT Epoxy resins, preparation
 Epoxy resins, preparation
 RL: IMF (Industrial manufacture); PRP (Properties); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)
 (polyether-, aromatic; epoxy compound-oxetane active energy beam-curable compns. with low viscosity)

IT Sulfonium compounds
 RL: CAT (Catalyst use); USES (Uses)
 (triaryl derivs., hexafluorophosphates; epoxy compound-oxetane active energy beam-curable compns. with low viscosity)

IT 108-32-7, Propylene carbonate 104558-95-4, Cyacure UVI 6990
 RL: CAT (Catalyst use); USES (Uses)
 (epoxy compound-oxetane active energy beam-curable compns. with low

DERWENT-ACC-NO: 1999-367209

DERWENT-WEEK: 199933

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TITLE: Active energycuring composition - comprises oxetane compound, compound containing at least two epoxy groups and cationic photopolymerisation initiator

PATENT-ASSIGNEE: TOA GOSEI CHEM IND LTD[TOAG]

PRIORITY-DATA: 1997JP-0316401 (October 31, 1997)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAINIPC
<u>JP 11140279 A</u>	May 25, 1999	N/A	006	C08L 063/00

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
JP 11140279A	N/A	1997JP0316401	October 31, 1997

INT-CL (IPC): C08G059/68, C08K005/15, C08L063/00

ABSTRACTED-PUB-NO: JP 11140279A

BASIC-ABSTRACT:

An active energy-curing compsn. comprises an oxetane cpd. of formula (1), a cpd. bearing at least two epoxy gps. in the mol. and a cationic photopolymerisation initiator. R1=methyl or ethyl.

USE - The active energy-curing compsns. are useful for coatings for woodwork, plastics, metals and paper, gloss varnishes, potted cpds., printing inks, sealants, adhesives, photoresists, wire insulating materials, coatings for protection, ornamentation, insulation and fabrics, laminates, impregnated tapes and printing plates.

ADVANTAGE - The active energy-curing compsns. have a low viscosity and cures by irradiation of an active energy such as an UV light and an electron beam rapidly to give a cured compsns. with excellent strength and elongation.

CHOSEN-DRAWING: Dwg.0/0

TITLE-TERMS: ACTIVE ENERGY CURE COMPOSITION COMPRISE OXETANE COMPOUND COMPOUND
CONTAIN TWO EPOXY GROUP CATION PHOTOPOLYMERISE NITATE

DERWENT-CLASS: A21 A81 A82 G02 G03

CPI-CODES: A05-A01B1; A08-D01; A11-C02; G02-A02G; G02-A04A; G03-B02E2;
G04-B02; G06-D04;

ENHANCED-POLYMER-INDEXING:

Polymer Index [1.1]

018 ; D18*R ; P0464*R D01 D22 D42 F47

Polymer Index [1.2]

018 ; G1570*R G1558 D01 D11 D10 D23 D22 D31 D42 D50 D69 D73 D83
F47 7A ; R00470 G1161 G1150 G1149 G1092 D01 D11 D10 D19 D18 D32
D50 D76 D93 F32 F30 ; H0022 H0011 ; P1898*R P0464 D01 D10 D11 D18
D19 D22 D42 D76 F34 F47 ; P047

Polymer Index [1.3]

018 ; ND04 ; ND01 ; B9999 B4988*R B4977 B4740 ; B9999 B4386 B4240
; K9869 K9847 K9790 ; K9814 K9803 K9790 ; K9790*R ; Q9999 Q7114*R
; Q9999 Q7170 Q7158 Q7114 ; K9552 K9483 ; K9574 K9483 ; K9609 K9483

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the activity energy-line hardening setup-of-tooling product which hardens promptly by the exposure of activity energy lines, such as ultraviolet rays or an electron ray, by hypoviscosity, and is excellent in the reinforcement and elongation of a hardened material.

[0002]

[Description of the Prior Art] The activity energy-line hardening setup-of-tooling product has been broadly used in coatings, such as paper, timber, plastics, and a metal, and various industries, such as ink for printing, from various properties, such as the quick cure rate, good workability by generally being a non-solvent, and a very low energy requirement. The oligomer of an acrylate (meta) system is used as a typical compound currently conventionally used in this field.

[0003] However, it was the object which raises the hardenability at the time of irradiating an activity energy line in many cases, since the polyfunctional (meta) acrylate which contains two or more acryloyl (meta) radicals in 1 molecule was being used for the constituent which used the oligomer of the conventional acrylate (meta) system, its hardening paint film obtained was hard, and there were few elongation percentages in many cases. Therefore, when it considered as a hardening paint film, shock resistance ran short, and there was a case where exfoliation, a crack, etc. of a paint film arose without the ability following processing of bending of a base material etc. In order to improve the flexibility of a hardening paint film conventionally, the urethane (meta) acrylate which is excellent in the elongation percentage of a hardening paint film was used together in many cases, but coating nature was inadequate, also when it has a problem to coating nature and used as a combination system, since urethane (meta) acrylate had very high viscosity. Moreover, although the monofunctional (meta) acrylate of low molecular weight may be blended with a constituent in order to improve the flexibility of a hardening paint film, the reinforcement of the hardening paint film obtained in this case fell, and there was a fault that a paint film became weak.

[0004] Moreover, the constituent of the optical cationic polymerization system hardened by optical cationic polymerization has also been examined in recent years as activity energy-line hardening setup-of-tooling products other than acrylate (meta). However, the paint film which the compound used there has many objects which do not have elongation firmly as hardened material physical properties because of the compound with which the many have two or more reactant radicals in 1 molecule, and is supplied is not obtained until now. Moreover, hardenability is dramatically inferior although a monofunctional epoxy compound like phenyl glycidyl ether may also be used.

[0005]

[Problem(s) to be Solved by the Invention] The object of this invention is hypoviscosity and is offering the activity energy-line hardening setup-of-tooling product which gives an unprecedented flexible hardened material.

[0006]

[Means for Solving the Problem] this invention persons came to complete a header and this invention for it being effective to use together a specific oxetane compound and a specific epoxy compound, as a result of inquiring wholeheartedly in view of such the actual condition. This invention is explained to a detail below.

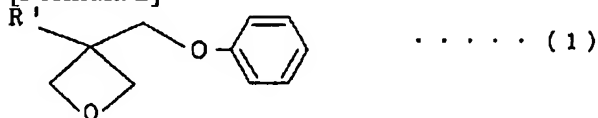
[0007]

[Embodiment of the Invention] This invention is explained below at a detail.

O The oxetane compound used by oxetane compound this invention is a compound (only henceforth an oxetane compound) expressed with the following general formula (1).

[0008]

[Formula 2]



[0009] However, it sets at a ceremony (1) and is R1. They are a methyl group or an ethyl group.

[0010] O As a compound (only henceforth an epoxy compound) which has two or more epoxy groups, both a monomer and its oligomer can be used into the compound molecule which has two or more epoxy groups in a molecule. As an example of the compound concerned, a well-known aromatic series epoxy compound, an alicycle group epoxy compound, and an aliphatic series epoxy compound are mentioned conventionally. In addition, an epoxy compound means a monomer or its oligomer below.

[0011] A thing desirable as an aromatic series epoxy compound It is JI or poly glycidyl ether obtained by the reaction of the polyhydric phenol which has at least one aromatic series nucleus, or its alkylene oxide adduct and epichlorohydrin. For example, JI or poly glycidyl ether of bisphenol A or its alkylene oxide adduct, JI or poly glycidyl ether of hydrogenation bisphenol A or its alkylene oxide adduct, JI or poly glycidyl ether of Bisphenol F or its alkylene oxide adduct, JI or poly glycidyl ether of the hydrogenation bisphenol F or its alkylene oxide adduct, A phenol novolak or the poly glycidyl ether of the alkylene oxide adduct and a cresol novolak, or the poly glycidyl ether of the alkylene oxide adduct is mentioned. Ethyleneoxide, propylene oxide, etc. are mentioned as alkylene oxide here.

[0012] The cyclohexene oxide or the cyclopentene oxide content compound therefore obtained is desirable for carrying out epoxidation of the compound which has cycloalkane rings, such as a KISEN ring or a cyclopentene ring, to at least one cyclo with suitable oxidizers, such as a hydrogen peroxide and a peroxy acid, as an alicycle group epoxy compound, and the compound shown by the following type (2) and (3) is mentioned to it as an example.

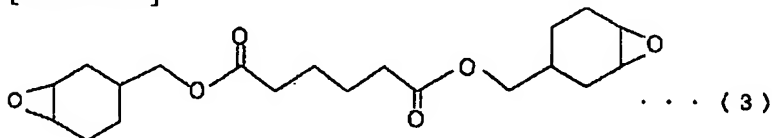
[0013]

[Formula 3]



[0014]

[Formula 4]



[0015] As a desirable thing of an aliphatic series epoxy compound There is JI or poly glycidyl ether of aliphatic series polyhydric alcohol or its alkylene oxide adduct etc. as the example of representation Ethylene glycol, a diethylene glycol, triethylene glycol, A polyethylene glycol, propylene glycol, dipropylene glycol, Tripropylene glycol, a polypropylene glycol, butanediol, Aliphatic series polyhydric alcohol, such as pentanediol, hexandiol, a glycerol, trimethylol propane, pentaerythritol, a SOROBİ toll,

and sorbitan, or the poly glycidyl ether of those alkylene oxide adducts is mentioned. Ethyleneoxide, propylene oxide, etc. are mentioned as alkylene oxide here.

[0016] As an epoxy compound, an aromatic series epoxy compound is desirable from the field of the reinforcement of a hardened material.

[0017] In this invention, two or more kinds of epoxy compounds can be used together.

[0018] O An optical cationic initiator light cationic initiator is a compound which makes cationic polymerization start by the exposure of an activity energy line. Various compounds can be used as an optical cationic initiator used with the constituent of this invention. As a desirable thing, a diaryl iodonium salt and a triarylsulfonium salt are mentioned among these initiators. A typical optical cationic initiator is shown below.

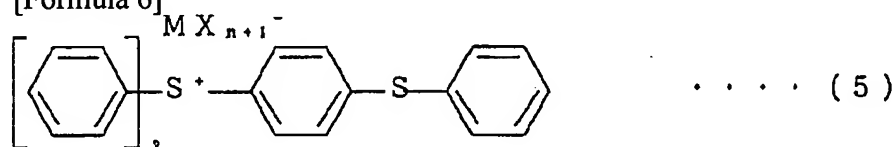
[0019]

[Formula 5]



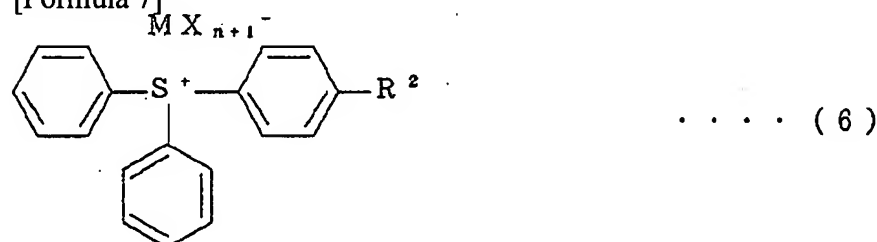
[0020]

[Formula 6]



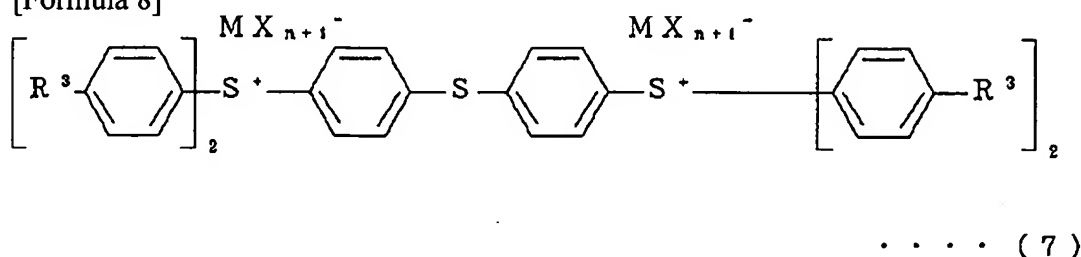
[0021]

[Formula 7]



[0022]

[Formula 8]



[0023] In addition, it sets at each above-mentioned ceremony, and is R2. It is hydrogen, the alkyl group of carbon numbers 1-18, or the alkoxy group of carbon numbers 1-18, and is R3. It is hydrogen, a hydroxyalkyl radical, and a hydroxy alkoxy group, and is a hydroxy ethoxy radical preferably. M is antimony preferably with a metal, X is a fluorine preferably by the halogen atom, and n is a metaled valence, for example, in the case of antimony, it is 6.

[0024] O What is necessary is just to determine the content rate of an oxetane compound and an epoxy compound in the constituent of content rate this invention in consideration of the viscosity of the constituent demanded, the degree of hardness of a hardened material, etc. As a desirable content rate of

an oxetane compound, it is 5 - 99 weight section to the total quantity 100 weight section of the oxetane compound in a constituent, and an epoxy compound, and is 30 - 95 weight section more preferably. When the flexibility of a hardening paint film becomes inadequate when the blending ratio of coal of an oxetane compound does not fulfill 5 weight sections and it exceeds the another side 99 weight section, hardenability may fall.

[0025] The desirable content rate of an optical cationic initiator is 0.1 - 20% of the weight of a rate to the total quantity of an oxetane compound and an epoxy compound, and is 0.1 - 10 % of the weight more preferably. Hardenability becomes inadequate, when not filling to 0.1% of the weight, when, exceeding 20 % of the weight on the other hand, light transmission nature becomes poor, uniform hardening may not be able to be performed or the smooth nature of a hardening paint film front face may be lost.

[0026] O Inerts like a cation reactivity compound like a monofunctional epoxy compound, oxetane compounds other than the above, and a vinyl ether compound, etc. an inorganic bulking agent, a color and a pigment, a viscosity modifier, a processing agent, and an ultraviolet-rays cutoff agent can be blended with the constituent of other component this inventions if needed besides the above-mentioned indispensable component.

[0027] When stiffening the constituent of this invention by the light or ultraviolet rays, in addition to an optical cationic initiator, a photosensitizer can also be blended in order to improve hardenability further. For the typical sensitizer which can be used in this invention, Crivello is ADOBANSUDO. Inn Polymer science (62 Adv.in Plymer Sci., 1 (1984)) It is possible to use the compound currently indicated. Specifically, there are a pyrene, perylene, an acridine orange, a thioxan ton, 2-chloro thioxan ton, a PENZO flavin, etc.

[0028] O What is necessary is just to mix an oxetane compound, an epoxy compound, and an optical cationic initiator according to a conventional method as the manufacture approach of the activity energy-line hardening setup-of-tooling product of manufacture approach this invention.

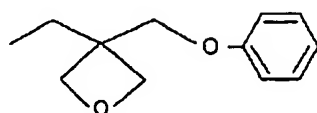
[0029] O Harden the constituent of the fast curability of operation this invention easily by irradiating activity energy lines, such as a visible ray, ultraviolet rays, and an electron ray. When irradiating ultraviolet rays, various light sources can be used, for example, it can be made to harden by a mercury lamp, a metal halide lamp, a xenon arc lamp, the fluorescent lamp, the carbon arc lamp, the tungsten-halogen copy lamp, and the exposure light from the sun. When irradiating ultraviolet rays, the exposure reinforcement to a base material is a 0.01 W square centimeter at least, and it is desirable to harden continuously with paper or a metal coating line by hardening a constituent within 1 - 20 seconds. Although it is made to usually harden with the electron ray of the following 300eV energy when making it harden with an electron ray, it is possible to also make it harden with the dose of 1Mrad - 5Mrad in an instant. The constituent of this invention is applicable to base materials, such as a metal, rubber, plastics, shaping components, a film, paper, a tree, a glass fabric, concrete, and a ceramic. As an application of the constituent of this invention, the coating for carpenters, the coating for plastics; the coating for metals, the coating for papers, gloss varnish, protection, an ornament and coating for an insulation, the coating for optical fibers, a **** compound, printing ink, a sealant, adhesives, a photoresist, a wire insulating material, textile coating, a lamination, an impregnated tape, a printing plate, etc. are mentioned, for example.

[0030]

[Example] An example and the example of a comparison are given to below, and this invention is more concretely explained to it. In addition, the section in an example and the example of a comparison is the weight section as long as there is no notice especially.

[0031] O As an example 1 oxetane compound, Union Carbide 6990 [CYRACUREUVI-] were 2-sections-added into the mixture of the diglycidyl ether 25 section of bisphenol A, it mixed as an optical cationic initiator into it as the following (compound A) 75 section and an epoxy compound, and the activity energy-line hardening setup-of-tooling product was prepared. About the obtained constituent, viscosity, the tensile strength of a hardened material, and an elongation percentage were evaluated according to the following approaches. Those results are shown in a table 2.

[0032]

[Formula 9]
化合物 (A)

[0033] O It measured at 25 degrees C using the measurement E mold rotational viscometer of the assessment approach and viscosity.

[0034] - The test piece for the measurement tension tests of tensile strength and an elongation percentage was slushed in the shuttering which set the obtained constituent by the dumbbell No. 2 by 1mm in thickness, with the high-pressure mercury-vapor lamp of 60 W/cm, carries out the UV irradiation (3500 mJ/cm²) of what was put with the PET film, stiffened it, and was created. A tension test is JIS. K It carried out according to 7113. In addition, the speed of testing was performed by part for 10mm/.

[0035]

[A table 1]

	材料 化合物	硬化剤化合物	(メタ)アクリレート	光開始剤
実施例 1	化合物 (A) 90部	YD-128 10部	—	UVI-6990 2部
実施例 2	化合物 (A) 75部	YD-128 25部	—	UVI-6990 2部
実施例 3	化合物 (A) 75部	YDCN-704P 25部	—	UVI-6990 2部
比較例 1	—	—	M-5700 75部 SP-1509 25部	Irg651 1部
比較例 2	—	—	M-5700 85部 M-1310 15部	Irg651 1部
比較例 3	—	EX-141 75部 YD-128 25部	—	UVI-6990 2部

[0036] In addition, the code in a table 1 shows following semantics.

- YD-128 : bisphenol A mold epoxy compound (the Tohto Kasei make, molecular weight about 380 and 2 organic-functions epoxy compound)
- YDCN-704P : cresol novolak mold epoxy compound (the Tohto Kasei make, molecular weight 2000 [about], polyfunctional epoxy compound)
- **M-5700: 2-hydroxy-3-phenoxypropylacrylate (Toagosei make)
- SP-1509 : bisphenol A mold epoxy acrylate (Showa High Polymer make)
- **M-1310: Urethane acrylate (Toagosei make)
- EX-141 : phenyl glycidyl ether (made in formation [Nagase Brothers])
- UVI-6990 : the hexa fluorophosphoric acid salt of triaryl sulfonium, and mixture of propylene

carbonate (made in Union Carbide)

- Irg651 : benzyl dimethyl ketal (Ciba-Geigy make)

[0037]

[A table 2]

	粘度 ($\text{mPa} \cdot \text{s}/25^\circ\text{C}$)	引張強度 (kgf/cm^2)	伸び率 (%)
実施例 1	2 3	9 5	2 1 0
実施例 2	4 7	1 9 0	6 0
実施例 3	2 0 0	1 9 5	6 5
比較例 1	8 4 0	5 6 0	7
比較例 2	1 0 4 0	1 7	1 9 0
比較例 3	1 7	未硬化	

[0038] O The constituent was manufactured like the example 1 except having changed, as the presentation of an example 2, these 3 oxetane compounds, and an epoxy compound was shown in a table 1. The obtained constituent was similarly estimated as the example 1. Those results are shown in a table 2.

[0039] O The constituent was manufactured like the example 1 except having changed, as the example 1 of a comparison - 3 each component were shown in a table 1. The obtained constituent was similarly estimated as the example 1. Those results are shown in a table 2.

[0040]

[Effect of the Invention] The activity energy-line hardening setup-of-tooling product of this invention is hypoviscosity, and since it excels in the flexibility of a hardened material, the effect which can use for various applications, such as the coating for carpenters, the coating for plastics, the coating for metals, the coating for papers, gloss varnish, protection, an ornament and coating for an insulation, the coating for optical fibers, a **** compound, printing ink, a sealant, adhesives, a photoresist, a wire insulating material, textile coating, a lamination, an impregnated tape, and a printing plate, and it has on the industrial world is size

[Translation done.]

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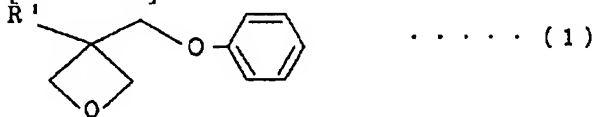
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CLAIMS

[Claim(s)]

[Claim 1] The activity energy-line hardening setup-of-tooling product which comes to contain the oxetane compound expressed with the following general formula (1), the compound which has two or more epoxy groups in a molecule, and an optical cationic initiator.

[Formula 1]



However, it sets at a ceremony (1) and is R1. They are a methyl group or an ethyl group.

[Claim 2] The activity energy-line hardening setup-of-tooling product according to claim 1 whose compound which has two or more epoxy groups in a molecule is an aromatic series epoxy compound.

[Translation done.]